Monitoring acetic acid vapour concentrations during fumigation of fruit for control of post harvest decay

P. Sholberg, T. Shephard and L. Moyls

Pacific Agri-Food Research Centre, Agriculture and Agri-Food Canada, Summerland, British Columbia, Canada V0H 1Z0.

Contribution No. 2,171.

Monitoring acetic acid vapour concentrations during fumigation of fruit for control of post harvest decay. Canadian Biosystems Engineering/Les génie des biosystèmes au Canada 45: 3.13-3.17. A fumigation technique using brief exposure of fruit to acetic acid (AA) vapour reduces post harvest decay if levels of AA are not exceeded that damage the crop. Two methods of monitoring AA vapour concentrations during fumigation are evaluated in this study. The first method uses a gas chromatograph (GC) for monitoring AA intermittently during fumigation. This method can be used to establish AA guidelines for fumigating fruit. For example it was determined that concentrations above 0.6 mg/L (224 ppm (v/v)) could blacken pears rendering them worthless. The second method relies on solid-state gas sensors to continuously monitor AA. An initial study with a methyl bromide gas sensor (International Sensor Technology, Irvine, CA), recalibrated to read AA, correlated reasonably well with the GC method but did not give a linear response from 0 to 1000 ppm (2.68 mg/L). In more recent studies, more advanced sensors (Model 4-20IQ and SM95) were evaluated. These sensors gave a linear response over the entire range from 0 to 1500 ppm AA. If these sensors could be manufactured so they would not easily lose their calibration, they could be used to maintain safe levels of AA during fumigation. Keywords: Blue mold, Botrytis cinerea, Gray mold, Penicillium expansum, post harvest decay, storage rot.

Une technique de fumigation employant la brève exposition à la vapeur d’acide acétique (AA) réduit la présence de pourriture post-récolte si on n’excède pas des niveaux d’AA qui endommagent la récolte. Deux méthodes de suivi des concentrations de vapeur d’AA pendant la fumigation sont évaluées dans cette étude. La première méthode utilise un chromatographe en phase gazeuse (CG) pour suivre les niveaux d’AA dans la chambre. Cette méthode peut être employée pour évaluer le contenu de la chambre d’AA à partir des mesures prises en continu pendant la fumigation. Cette méthode a été utilisée pour évaluer la corrélation entre la concentration de AA et la quantité de pourriture. En plus, des études plus récentes ont été effectuées avec des capteurs à semi-conducteurs de gaz qui surveillent la concentration en AA. Ces capteurs ont donné une relation linéaire entre la concentration en AA et la quantité de pourriture. Si ces capteurs pourraient être fabriqués de façon à ce qu’elles ne perdent pas facilement leur calibrage, elles pourraient être utilisées pour maintenir des niveaux sûrs d’AA pendant la fumigation.

INTRODUCTION

Fumigants are particularly useful in controlling pests because the fumигант can diffuse through space and penetrate into protected places that are inaccessible to liquid or solid pesticides (Bond 1973). The only commercial crop as far as we are aware, fumigated to prevent decay are table grapes. Packed boxes of grapes are placed on pallets in the field and brought to a cold storage facility where they are immediately fumigated with sulphur dioxide and precooled (Luvisi et al. 1992). Grapes kept for long term storage are kept in separate rooms at -0.5°C where they are fumigated weekly until they are sold. Sulphur dioxide fumigation of table grapes to prevent the spread of the fungus Botrytis cinerea from grape to grape has been successfully practiced for at least 80 years. It has always been a balancing act between the need to maximize decay control and minimize fruit bleaching. The amount of sulphur dioxide needed to control B. cinerea is close to the concentration that causes some bleaching to the fruit (Smilanick and Henson 1992). Several other fumigants have been evaluated for decay control over the years but have not been adapted for commercial use (Sholberg et al. 1998). More recently, acetic acid vapour in pure form (Sholberg et al. 1998) or as vinegar (Sholberg et al. 2000) has been shown to be a very effective treatment for reducing post harvest decay.

Early fumigation trials with AA were conducted in small 13-L containers on apples, grapes, kiwifruit, pears, tomatoes (Sholberg and Gaunce 1995), and stone fruit (Sholberg and Gaunce 1996a) to prevent post harvest decay caused by Botrytis cinerea, Penicillium expansum or Monilinia fructicola. The AA concentration in the chamber was not monitored during fumigation. It soon became apparent that AA vapour concentrations did not need to be very high to blacken and damage fruit tissue. Stone fruit were extremely sensitive to AA vapour and peaches displayed symptoms of phytotoxicity when fumigated with acetic acid concentrations higher than 2.0 mg/L (746 ppm (v/v))(Sholberg and Gaunce 1996a). Blackened stems and pitting were recorded on cherry and streaking was recorded on apricots, peaches, and nectarines fumigated with 2.0 mg/L AA vapour (Sholberg 1998). On the other hand, if AA concentrations were below critical levels that killed fungal spores on fruit there would be no beneficial effect and the fumigation would be a waste of time. For these reasons, it became necessary to accurately monitor AA vapour during fumigation.
Early on in the development of AA for use in control of post harvest decay it became apparent that the several methods of measuring acetic acid concentration during fumigation had particular strengths and weaknesses. The first method tested by our laboratory involved the use of gas-sensitive detector tubes. These tubes were used to monitor acetic acid vapour or sulphur dioxide gas in a study on fumigation of table grapes for post harvest decay control (Sholberg et al. 1996). The tubes were sensitive to acetic acid and did a good job of detecting the vapour at low concentrations but could not be used to monitor the vapour over the duration of the fumigation because of their limited range (0-50 ppm). They could be modified to read higher concentrations but were expensive and cumbersome to use.

The use of gas chromatography to monitor hazardous gases has fast response and good sensitivity with detection limits in the low ppm ranges for hydrocarbon gases (Chou 2000). The GC consists of a column for separation of gas components and a detector to identify and quantify the gases. A GC was first used by this laboratory to monitor AA during fumigation of high moisture seed to control storage mold (Sholberg and Gaunce 1996b). The GC had a photo-ionization detector calibrated by sampling a series of known concentrations of AA in a 4-L glass reagent bottle. The use of this GC was discontinued because of difficulties with calibration of the instrument and occasional unexplained peaks produced by the instrument.

Many years ago, during research on semiconductors, it was discovered that the p-n junctions were sensitive to background gases. The first solid-state sensors useful for the detection of more than 100 different hazardous gases at low ppm levels were developed by International Sensor Technology in the early 1970's. Solid-state sensors for monitoring gases such as acetic acid vapor consist of one or more metal oxides that causes the gas to dissociate into charged ions (Chou 2000). The changes in the conductivity of the sensor resulting from the interaction with the gas molecule is measured as a signal. The solid-state sensor has the ability to detect both low and high ppm levels of gases.

The object of this study was to develop reliable methods for monitoring AA vapour during fumigation of produce. For this purpose two methods were evaluated, one that monitored AA vapour concentrations intermittently over time by sampling gas directly and injecting into a GC with a flame ionization detector and a second method that continuously monitored AA vapour concentrations with a solid-state sensor tuned for acetic acid. It also was important to determine if the test method could be used to control the fumigation process so that the acid concentration could be maintained at levels that were safe for produce while destroying the organisms that caused decay.

MATERIALS and METHODS

GC analysis of acetic acid vapour

Known concentrations of glacial acetic acid from 0 to 10 mg/L were vaporized in a 4-L glass bottle and used to calibrate the GC. The GC used for monitoring acetic acid vapour concentrations was a HP5840A (Hewlett Packard, Mississauga, ON). The GC was outfitted with an FID detector and fused silica capillary column, DB®-FFAP, 15 m x 0.32 mm, 0.25 μm film thickness (J&W Fused Silica column, Chromatographic Specialties Inc., Brockville, ON). The operating conditions for the GC were 130°C for the column and 250°C for the detector with ambient injection temperature. The carrier gas was helium with a flow rate of 1 mL/min. Gas samples were obtained either with a syringe (Hamilton, Model 725, Reno, NV) or a 250 mL sampling bulb (Mandel Scientific, Guelph, ON) and injected into the GC. The GC was used to monitor AA during fumigation of harvested Anjou pears each fall from 1998 until 2000. Most of the fumigations were done at 2°C in a 3 x 2.5 x 3.6 m refrigerated room originally designed for methyl bromide fumigation. AA was vaporized by pumping laboratory grade glacial acetic acid at 20°C into an aluminum frying pan set at 120°C. Higher temperatures should be avoided because concentrated acetic acid in air will auto ignite and burn at 269°C. The action of AA is similar to sulphur dioxide (Luvisi et al. 1992) and can be described in terms of its concentration and the time it is in contact with the pathogen.

Solid-state analysis of acetic acid vapour

A solid-state sensor (International Sensor Technology, Irvine, CA) originally installed to detect 0-500 ppm methyl bromide (MBr) gas was converted to measure 0-2000 ppm (0.5-4 mg/L) AA vapor. Note that at standard conditions of pressure and temperature 1 mg/L AA equals 373 ppm. The ceramic semiconductor sensor has a current setting which is adjusted for specific gases. The current heats the ceramic which self cleans and prevents saturation with gas compounds. Zero and span ranges are field-adjustable by potentiometer. Higher current settings were required for AA vapor than MBr. The sensor was tested over a range of 250 to 1100 ppm (0.7-2.9 mg/L) in the room used for fumigation of Anjou pears and the results were compared to those from the GC. Data were analyzed with the Pearson correlation test from the Graphpad Software package (GraphPad Software, Inc., San Diego, CA).

Two newer model solid state sensors were obtained for testing AA gas concentrations. The model 4-20IQ (International Sensor Technology, Irvine, CA) has an integrated digital display so concentrations of gas in ppm can be read directly. It was calibrated to detect 0-2.5 mg/L AA vapor in air. The model SM95 (International Sensor Technology, Irvine, CA) does not have the display and the calibration settings are manual (Fig. 1). It is the same model that was used for MBr with some improvements. It was calibrated to detect 0-10 mg/L AA vapor in air. Both models operate on 14-24 VDC and produce a 4-20 mA linear output proportional to the gas concentration. These models were calibrated with AA vapor in a 23-L aluminum pot by adding AA to the pot and measuring the concentration with the calibrated GC.

RESULTS and DISCUSSION

Use of a gas chromatograph for monitoring acetic acid vapour in air

The gas chromatograph (GC) provided a linear relationship (R² = 0.998) of acetic acid concentration in ambient air over the range of 0 to 8 mg/L AA with the lower limit of detection at 0.5 mg/L. This showed that the GC would provide accurate measurement of AA in air during fumigation of various crops. Gas tight syringes used to transport gas samples from the fumigation room to the GC over short distances were prone to leakage. The situation was corrected by using gas sampling.
Fig. 1. Model SM95 sensor shown with its cover off to expose the electronic components. The transmitter or gas sensing mechanism is in the tube at the bottom of the sensor and must come in direct contact with acetic acid vapour.

Fig. 2. The ideal concentration of acetic acid vapour and time needed to control decay in pears as determined by over 100 fumigation trials monitored by GC. Note that if pears are exposed to 0.6 mg/L or higher AA vapour for more than 0.5 h, they will be damaged.

Use of a converted methyl bromide solid-state sensor for monitoring acetic acid vapour in air
The converted solid state sensor provided a non-linear response over the range of 0 to 2000 ppm (0-5.36 mg/L) AA (Fig. 3). Over the range of 0 to 400 ppm (0-1.1 mg/L) AA the response was linear but the sensor became saturated with high levels of AA causing the meter to indicate the presence of gas when none was in the fumigation chamber. Higher sensor current settings combat this effect but reduce sensitivity at the lower values. Sensor accuracy was close to the GC for the 0 to 1.0 mg/L range with a standard deviation of ±0.1 mg/L and correlated well with the GC results for Anjou pear fumigations in 1998 and 1999 (Table 1). This accuracy would be adequate for feedback control of an AA fumigation treatment of crops that are relatively tolerant of acetic acid such as strawberries (Moyls et al. 1996).

Use of modern solid state sensors for monitoring acetic acid vapour in air
The 4-20IQ solid state sensor was an improvement over the earlier model of sensor that was used for methyl bromide and converted to use for AA. It provided a linear response ($R^2 = 0.9948$) over the range of 0 to 1500 ppm (0 - 4.0 mg/L)

Table 1. Correlation of AA vapour concentration between GC and solid-state sensor results.

<table>
<thead>
<tr>
<th>Correlation parameters</th>
<th>Year of test</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1998</td>
</tr>
<tr>
<td>Number of xy pairs</td>
<td>43</td>
</tr>
<tr>
<td>Pearson r</td>
<td>0.8855</td>
</tr>
<tr>
<td>95% confidence interval</td>
<td>0.7971-0.9367</td>
</tr>
<tr>
<td>P value (two-tailed)</td>
<td>$P&lt;0.0001$</td>
</tr>
<tr>
<td>Correlation significant</td>
<td>yes</td>
</tr>
<tr>
<td>R-squared value</td>
<td>0.7840</td>
</tr>
</tbody>
</table>
Fig. 4. Response to acetic acid vapour concentration of the 4-20IQ sensor over the range 0-1000 ppm. The response was linear but needed to be offset to read zero acetic acid.

AA (Fig. 4). A problem experienced with this unit, however was the incorrect indication of the presence of AA at zero after the unit had been used to read high ppm values. This inaccurate reading was eliminated by zeroing the meter with 0.1 mg/L of AA, which then produced a linear response ($R^2 = 0.9888$) with y-intercept at zero (Fig. 4). The automatic calibration feature of the 4-20IQ did not function with AA under conditions of these trials so the SM-95 meter without automatic calibration is a more economical choice and its 4-20 mA signal can easily be interfaced with a computer-based data acquisition system for data logging and feedback control during fumigation with AA.

Comparing continuous application of acetic acid with timed applications

If the chamber is tightly packed with produce, AA is quickly absorbed, requiring multiple doses. Addition of acetic acid in large doses results in spikes in the concentration of acetic acid in the fumigation room (Fig. 5). Spikes like these can damage produce and do not always kill the pathogen. A more controlled approach would target a set value to be reached and be maintained automatically by adding small amounts of AA similar to control of relative humidity with water. Monitoring acetic acid continuously makes it possible to keep AA concentrations at or below 0.45 mg/L which will not cause damage to produce but will control surface-borne pathogens on most fruit and vegetable crops. Figure 5 shows the type of profile that is desirable for fumigation of produce with AA vapour. The feedback system requires the use of a pump that adds small amounts of AA to an evaporator heater.

CONCLUSIONS

Monitoring acetic acid concentration with a GC during fumigation of produce was more reliable than solid-state sensors. These sensors show promise for automatically controlling AA rates during fumigation by a feedback loop to increase or decrease the amount of acid added. Unfortunately they are not very robust and lose calibration rather easily. At the present time the GC is being used to produce rate guidelines for fumigation with AA that could be used in commercial operations.

Fig. 5. Acetic acid vapour concentration during uncontrolled and controlled application of AA. When AA is added without knowledge of concentration, spikes of high AA may damage the pears.

ACKNOWLEDGEMENTS

We gratefully acknowledge the financial support of Agriculture and Agri-Food Canada and Washington Tree Fruit Research Commission. We also thank Tony Cottrell for technical assistance on use of the GC and Julie Boulé for the French translation of the abstract.

REFERENCES


